ON PERSPECTIVES OF CO_2-FREE PPRODUCTION OF HYDROGEN FROM HYDROCARBON FUELS FOR SMALL SCALE APPLICATIONS

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ABSTRACT

All conventional options of hydrogen production from fossil fuels, primarily, natural gas (e.g. steam reforming, partial oxidation) are complex, multi-stage processes that produce large quantities of CO_2. In general, there are two ways to solve CO_2 emissions problem:
a) sequestration of CO_2 produced by the conventional methods of hydrogen production, and
b) decomposition (thermal, thermocatalytic, plasmochemical) of hydrocarbon fuels into hydrogen and carbon. The capture of CO_2 from the process streams and its sequestration (underground or ocean disposal) is costly, energy intensive, and poses uncertain ecological consequences. The main objective of this work is to develop a viable process for CO_2-free production of hydrogen via one-step thermocatalytic decomposition of hydrocarbon fuels into hydrogen and carbon. This process could be the basis for the development of compact units for on-site production of hydrogen from hydrocarbon fuels (e.g. natural gas and gasoline) at gas refueling stations. The concept can also be used for a CO_2-free production of hydrogen for fuel cell applications (mobile and stationary).

INTRODUCTION

In the near- to medium-term future hydrogen production will continue to rely on fossil fuels, primarily, natural gas (NG). For decades, steam reforming (SR) of NG has been the most efficient and widely used process for the production of hydrogen. Other conventional processes for hydrogen production from fossil fuels: partial oxidation (PO), autothermal reforming (AR), steam-oxygen gasification of residual oil and coal) are more expensive than SR. The SR of NG process basically represents a catalytic conversion of methane (a major component of the hydrocarbon feedstock) and water (steam) to hydrogen and carbon oxides, and consists of three main steps: a) a synthesis gas generation. b) water-gas shift reaction, and c) gas purification (CO_2 removal). Four moles of hydrogen are produced in the reaction with half of it coming from the methane and another half from water. The energy requirement per mole of hydrogen produced for the overall process is equal to 40.8 kJ/mole H_2. To ensure a maximum conversion of CH_4 into the products, the process generally employs a steam/carbon ratio of 3-5, the process temperature of 800-900°C and pressure of 35 atm. A steam reformer fuel usage is a significant part (up to 30-40%) of the total NG usage of a typical hydrogen plant. There is no by-product credit (except for steam) for the process and, in the final analysis, it does not look environmentally benign due to large CO_2 emissions. The total CO_2 emission from SR process reaches up to 0.4 m^3 per each m^3 of hydrogen produced. Heavy residual oil and coal based hydrogen production processes result in the emission of enormous volumes of CO_2 (up to 0.8 m^3 per m^3 of H_2). Therefore, the problem of large scale production of hydrogen from fossil fuels and its utilization as a major energy carrier in the near future will be tied up with the development of effective, economical and environmentally acceptable ways of managing CO_2 emissions. In general, there are two ways to solve the problem of CO_2 emissions:

* Sequestration of CO_2 produced by the conventional methods of hydrogen production from fossil fuels, and
* Decomposition (thermal, thermocatalytic, plasmochemical) of hydrocarbon fuels into hydrogen and carbon

CARBON SEQUESTRATION

The main purpose of carbon sequestration is to keep CO_2 emissions from reaching the atmosphere by capturing and diverting them to secure storage. The perspectives of CO_2 capture and sequestration (ocean or underground disposal) is actively discussed in the literature [1-3]. The commercially available processes for CO_2 separation and capture include: physical and chemical absorption, physical and chemical adsorption, low temperature distillation and gas-separation membranes. It should be noted, however, that the capture, transportation and sequestration of CO_2 are energy intensive and costly processes. Thus, according to [3], the capture and disposal of CO_2 add about 25-30% to the cost of hydrogen produced by the SR of NG. The total electric energy consumption to pressurize CO_2 to 80 bar, transport it 100-500 km and inject it to the underground disposal site is estimated at approximately 2000 kJ$_e$/kg CO_2. World average for CO_2

emission associated with the electricity production is 0.153 kg of CO_2 per each kWh produced [2]. Thus, the amount of CO_2 produced as a result of the capture of CO_2 from the concentrated streams (after pressure swing adsorption, PSA, unit) of SR process and its sequestration reaches up to 0.1 kg per kg of sequestrated CO_2. In principle, CO_2 can also be captured from the stack gases of the hydrogen plant (where it is presented in a highly diluted form) and sequestrated, however, the energy cost of this operation would be very high. For example, it was estimated that the cost of eliminating CO_2 emissions from stack gases of advanced power generation plants range from \$35 to 264 per ton of CO_2 [4]. It was also estimated that the costs of CO_2 separation, capture, and compression to the required pressure would make up about three fourths of the total cost of ocean or geologic sequestration [5]. According to [6], the energy consumption associated with CO_2 recovery from the stack gases by hot K_2CO_3 solutions amounts to 3000 kJ/kg CO_2. In consequence, the total CO_2 emissions from CO_2 capture, transportation, and underground disposal could easily reach 0.25 kg CO_2 per kg of sequestrated CO_2. Thus, CO_2 sequestration is an energy intensive process and, in the final analysis, does not completely eliminate CO_2 emission. In addition to this problem, some uncertainties remain regarding the duration and extent of CO_2 retention (underground or under the ocean) and its possible environmental effect.

THERMOCATALYTIC PYROLYSIS OF HYDROCARBON FUELS

Thermal (thermocatalytic) decomposition (pyrolysis) is the most radical way for a CO_2-free production of hydrogen from hydrocarbons, particularly, NG:

$C_nH_m \rightarrow nC + m/2H_2$

$CH_4 \rightarrow C + 2H_2 + 75.6$ kJ
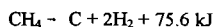
The energy requirement per mole of hydrogen produced from methane (37.8 kJ/mole H_2) is somewhat less than that for the SR process. The process is slightly endothermic so that less than 10% of the heat of methane combustion is needed to drive the process. The process is environmentally compatible, as it produces relatively small amounts of CO_2 (approximately 0.05 m^3 per m^3 of H_2 produced, if CH_4 is used as a fuel). It should be noted, however, that the process could potentially be completely CO_2-free if a relatively small part of hydrogen produced (approximately 14%) is used as a process fuel. In addition to hydrogen as a major product, the process produces a very important by-product: clean carbon. Currently, the total world production of carbon black is close to 6 mln tons per year, with prices varying in the range of hundreds to thousands dollars per ton, depending on the carbon quality [7]. The carbon black has a great market potential both in traditional (rubber industry, plastics, inks, etc.) and new areas.

Low pressure and high temperatures (up to 1400°C) are favorable for the complete thermal decomposition of methane. Attempts have been made to use catalysts to reduce the maximum temperature of the decomposition of various hydrocarbon fuels. In [8], for example, the authors used alumina, silica-alumina, silica-magnesia and other contacts at 800-1000°C for decomposition of NG and light hydrocarbons. The data on the catalytic decomposition of methane using Co, Cr, Ni, Fe, Pt, Pd and Rh-based catalysts have also been reported in the literature [9, 10]. In all cases, carbon produced was burned off the catalyst surface to regenerate its initial activity. In this regard, these processes display no significant advantages over the conventional processes (for example, SR) because of large CO_2 emissions.

The main objective of our work is to develop a thermocatalytic process for the simultaneous production of hydrogen and carbon from different hydrocarbon fuels (NG, liquid hydrocarbons) [11-13]. The use of carbon-based catalysts offers significant advantages over metal catalysts since there is no need for the separation of carbon from the catalyst surface: carbon produced builds up on the surface of the original carbon catalyst and can be continuously removed from the reactor (for example, using a fluidized bed reactor). There is a lack of information in the literature on the catalytic properties of various forms and modifications of carbon in methane decomposition reaction. We determined the catalytic activity of various carbon materials (graphite, carbon black, different types of activated carbon) for methane decomposition reaction over the range of temperatures from 700 to 900°C. It was found that the activated carbon produced from coconut shells displayed the highest initial activity among other forms of carbon, producing gas with hydrogen concentration up to 70-75%v at 850°C. In all cases, there were no methane decomposition products other than hydrogen and carbon and traces of ethane and ethylene detected in the effluent gas. Poor performance of the graphite and carbon black catalysts can be explained by the structure and size of carbon crystallites.

From the thermodynamic point of view the pyrolysis of liquid hydrocarbons is more favorable than the decomposition of methane, as almost 1.5-2 times less energy is required to produce a unit volume of hydrogen. We studied catalytic pyrolysis of a wide range of liquid hydrocarbons (pentane, hexane, octane, gasoline and diesel fuel) using different carbon-based catalysts. In the presence of activated carbon (coconut) the steady state pyrolysis of liquid hydrocarbons was achieved over period of approximately one hour. For example, gasoline pyrolysis over activated carbon (coconut) at 750°C produced gas consisting mainly of hydrogen (45-50 v.%) and methane (40-45 v.%) with relatively small fraction of C_2+ hydrocarbons (<10 v.%). The gas production rate reached 650 mL/min per mL/min of gasoline. In the case of diesel fuel the concentrations of hydrogen and methane in the effluent gas were in the range of 25-30 and 35-40 v.%, respectively (balance: C_2^+ hydrocarbons).

COMPARATIVE ASSESSMENT OF DIFFERENT HYDROGEN PRODUCTION PROCESSES

Thermocatalytic pyrolysis (TP) of NG is a technologically simple one-step process without energy and material intensive gas separation stages, while SR is a multi-step and complex process. The techno-economic assessment showed that the cost of hydrogen produced by thermal decomposition of NG ($58/1000 m^3 H_2, with carbon credit), is somewhat lower than that for the SR process ($67/1000 m^3 H_2) [14].

The decomposition of methane can also be carried out plasmochemically. In a paper [7], the authors advocated a plasma-assisted decomposition of methane into hydrogen and carbon. It was estimated that up to 1.9 kWh of electrical energy is consumed per one normal cubic meter of hydrogen produced. Since almost 80% of the total world energy supply is based on fossil fuels [1], one can expect the electricity-driven hydrogen production processes to be among major CO_2 producers. A comparative assessment of the hydrogen production by SR, without and with CO_2 (after PSA unit) sequestration, electrolysis, plasmochemical decomposition (PD) and TP (with CH_4 and H_2 as a process fuel options) of NG is depicted on Figure. The comparison is based on two very important parameters, which reflect the energetic and ecological features of the processes. The first parameter (En) is equal to the total volume of NG consumed (both as a feedstock and a fuel) for the production of a unit volume of H_2 (En =NG/H_2, m^3/m^3). The second parameter (Ec) is equal to the total volume of CO_2 produced from both the feedstock and fuel usage of NG per a unit volume of H_2 produced (Ec= CO_2/H_2, m^3/m^3). Evidently, the lesser are both En and Ec parameters, the better is a hydrogen production process. For the sake of simplicity and comparability, it was assumed that NG was the primary fuel (at the power plant) for the water electrolysis and PD of NG. In fact, this assumption leads to rather conservative value for Ec parameter since NG share in total energy supply is only 19% and, what is more, NG produces 1.9 and 1.7 times less CO_2 (per kWh produced) than oil and coal, respectively [1]. The following conclusions can be extracted from Figure.

1. The processes with the large consumption of electric energy (water electrolysis, PD of NG) are characterized with the highest NG consumption and CO_2 emission per unit of hydrogen produced. It should be noted, however, that this conclusion is based on the world average energy production scenario, therefore, in countries with a large non-fossil fuel energy sector (hydroelectric, nuclear energy) both En and Ec parameters could be much lower.
2. SR with CO_2 capture (after PSA unit) and sequestration produces 30% less CO_2 emission than SR without CO_2 sequestration.
3. SR with CO_2 sequestration consumes 33% less NG than TP process, however, it produces 5 times more CO_2 emission.
4. TP of NG is the only fossil fuel based process which shows a real potential to be a completely CO_2-free hydrogen production process

SMALL SCALE HYDROGEN PRODUCTION UNITS

TP process does not include many material and energy intensive technological steps required by the conventional processes (SR, PO and AR), such as a two step water gas shift reaction, preferential oxidation, CO_2 removal, steam generation, etc. This is a significant advantage that TP holds over conventional processes, because it may potentially result in more simple, compact, and cost effective hydrogen production units. Based on our preliminary experimental data on gasoline pyrolysis, we project the volumetric power density of the TP-processor at approximately 0.8-1.0 kW_{th}/L. A comparative assessment of small scale hydrocarbon fuel processors based on SR, PO, PD and TP processes is presented in the Table.

There are several potential uses for the TP-based fuel processor (TPP):

1. The TPP can be used for on-site production of hydrogen at gas filling stations. TPP directly converts natural gas (or other hydrocarbon fuels) into methane-hydrogen blends, e.g HYTHANE™ (H_2:CH_4= 30:70 v.%/v.%) which can be used by ICE vehicles. Due to the flexibility of the TPP, it can produce different H_2-CH_4 mixtures in a single step, whereas, the conventional processes require 2 steps: initial production of hydrogen and then blending it with methane.

2. The TPP can be used in combination with fuel cells, for example, polymer electrolyte fuel cells (PEFC) for stationary applications (e.g. buildings, resort areas, etc.). It is known that PEFCs impose very stringent limitations on the level of CO impurity in the hydrogen feedstock ([CO]< 100 ppmv). TPP perfectly fits these requirements for it produces hydrogen that is completely free of carbon oxides.

3. The TPP can be combined with a PEFC for transportation applications. The TP process does not include bulky gas separation stages, and, therefore, leads to a compact fuel processor perfectly suited for on-board applications. On the other hand, mobile application of TPP is associated with the necessity for storing solid carbon on-board of a vehicle (approximately 3-8 kg per refueling, depending on feedstock).

4. Special CO_2-sensitive applications (space, mines, medicine, etc.).

One of the major issues associated with the proposed technology is related to a byproduct carbon. The amount of carbon produced at average gas filling station is estimated at approximately 250 kg per day (based on HYTHANE™ production from NG). A 10 kW TPP/PEFC power system is expected to produce approximately 0.7 kg/h of clean carbon. Carbon produced can be conveniently collected by special trucks, stored at the central collector and sold at reasonable prices.

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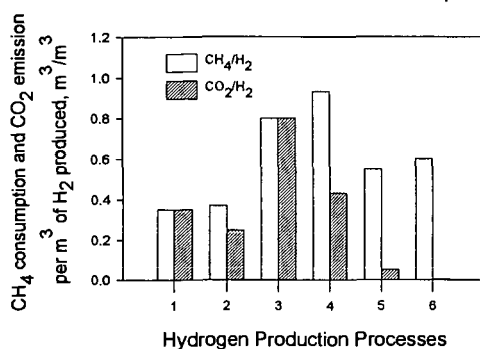
CH$_4$ consumption and CO$_2$ emission per m^3 of H$_2$ produced, m^3/m^3

1.2
1.0
0.8
0.6
0.4
0.2
0.0

□ CH$_4$/H$_2$
▨ CO$_2$/H$_2$

1 2 3 4 5 6

Hydrogen Production Processes

FIGURE. COMPARATIVE ASSESSMENT OF DIFFERENT
HYDROGEN PRODUCTION PROCESSES:
1- SR, 2- SR with CO$_2$ sequestration, 3- electrolysis,
4- PD, 5- TP (CH$_4$- fuel), 6- TP (H$_2$- fuel)

TABLE. COMPARATIVE ASSESSMENT OF HYDROGEN PRODUCTION
PROCESSES FOR SMALL SCALE APPLICATIONS

Process characteristics	Steam Reforming	Partial Oxidation	Plasmochem. Decompos.	Thermocatal. Pyrolysis
Capacity of small scale units, 10^3 m^3/h	0.1-5.9	0.02-4.0	2.0	N/A
Commercial availability	Yes	Yes	Yes	No
Number of steps	3	3	1	1
Maximum temperature, °C	850-900	1400	Plasma	800-900
Need for WGSR and CO$_2$ removal units	Yes	Yes	No	No
Special process requirements	Steam	Oxygen/Air	Electricity 1- 2 kWh per m^{3}H$_2$	None
Need for catalyst	Yes	No/Yes	No	Yes
Fuel flexibility	Low	High	Moderate	High
Tolerance to sulfur in a feedstock	Very low	High	Moderate	High
Useful byproduct	None	None	Carbon	Carbon
Efficiency, %	78.5	80	95	92.8[1]
Process CO$_2$ emission[2]	High	High	None	None[3]
Power density, kW/L (kW/kg)	0.9 kW/kg[4]	0.9 kW/kg[5]	4 kW$_e$/L	0.8-1 kW/L[6]

[1] - total efficiency with carbon as a byproduct;
[2] - does not include CO$_2$ generated at power plants
[3] - part of H$_2$ is used as a fuel
[4] - methanol steam reformer, [15]
[5] - PO of gasoline, [15]
[6] - based on our experimental data on TP of gasoline